

## ⊕ Entropy $S$

Obtained as above from

$$S = - \left( \frac{\partial F}{\partial T} \right)_V$$

$$F = -NkT \ln Z$$

Gives 
$$S = Nk \left\{ \ln \left( \frac{\exp(\frac{h\nu}{kT})}{[\exp(\frac{h\nu}{kT}) - 1]} \right) + \frac{(\frac{h\nu}{kT})}{[\exp(\frac{h\nu}{kT}) - 1]} \right\}$$

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Comparison to real systems.

1. Vibration of  $N$  atoms in solid.

Can change from 1D  $\rightarrow$  3D vibrations

by considering  $3N$  oscillators

Snag In solid atomic vib<sup>ns</sup> not independent.

Independent — just one freq  $\nu$

Coupled — range of freqs

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Nevertheless.

Have developed quantum mechanical model for vib<sup>n</sup> of atoms in solid.

Our approx — just one value  $\nu$

→ Einstein model.

(Range of  $\nu$  values — simplest treatment — Debye).

Einstein model.

Successes

(i) High temp value  $C_v \rightarrow 3Nk$

(ii) As  $T \rightarrow 0$   $C_v \rightarrow 0$

Failures

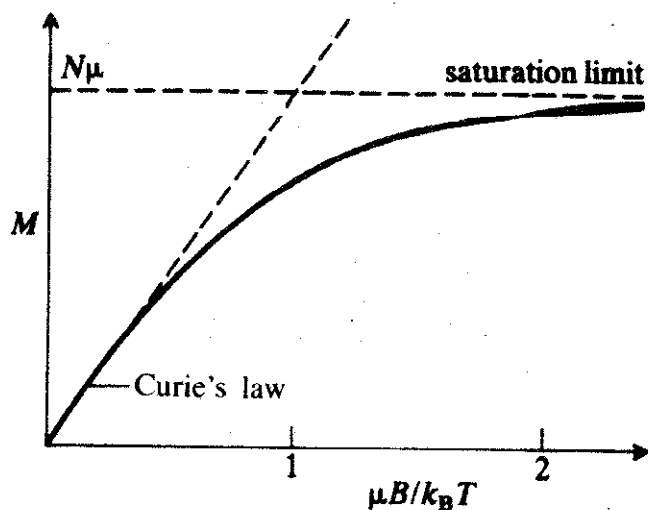
Does not predict correct shape for

$C_v$  versus  $T$  between above limits

Comparison — see sheet.

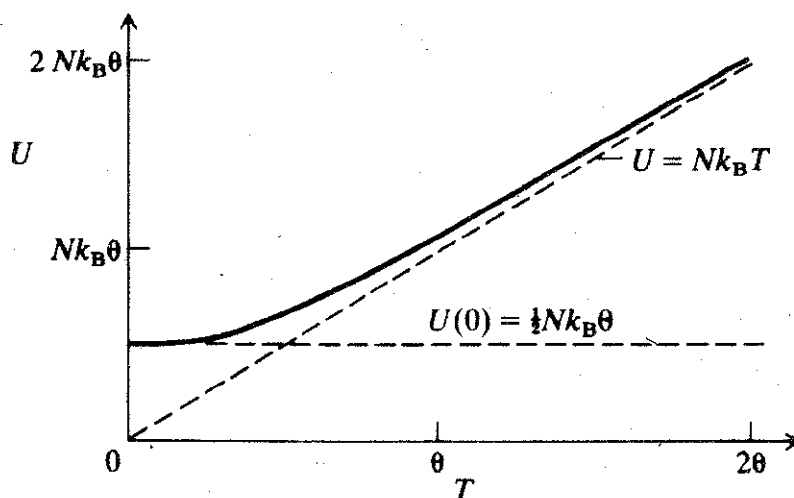
Paramagnetic solid

$M$  versus  $(\mu_B/kT)$

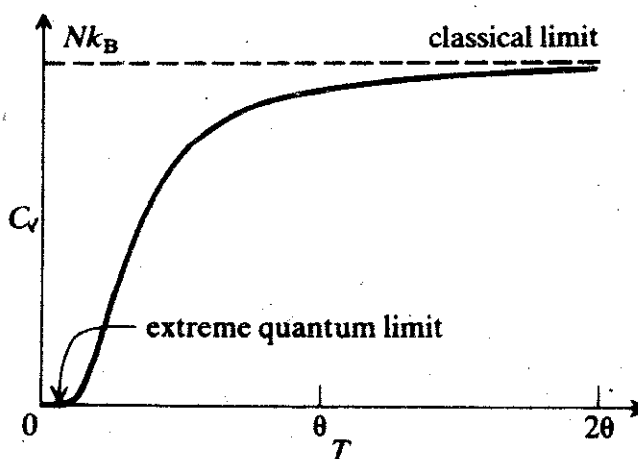


System of  $N$   
one dimensional  
oscillators.

Energy.



Heat Capacity



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## Quantum and classical limits

At temp  $T$  mean energy ration for each energy mechanism is  $kT$ .

But energy mechanisms have their own (quantised) energy scale.

Eg harmonic oscillator  $\epsilon = j h \nu$

$\nu$  depends on mechanical properties of oscillator.

Relation between  $\epsilon$  and  $kT$  determines quantum or classical behaviour.

(i) If  $\epsilon \gg kT$

$\epsilon = \underline{\hspace{2cm}}$

Quantum behaviour

most systems  $\epsilon = 0$

few  $\epsilon = \epsilon$

0  $\underline{\hspace{2cm}}$   $\underline{\hspace{1cm}}$   $\xleftarrow{kT}$

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(ii) If  $\epsilon \ll kT$



Classical limit  
 $\epsilon$  levels so closely  
packed they approach  
continuum.

In above analyses get changes in

$U, C_v, S$  when  $kT \sim \epsilon$

In reverse if measure  $C_v$  versus  $T$  -  
get features in graph at temp  $T$

where  $kT \sim$  energy level spacing.

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Non-localised particles.

Gases.

From quantum mechanics of particles in  
a box of side  $L$  — get  
expression for density of states

$g(\epsilon) d\epsilon =$  number of energy states  
between  $\epsilon \rightarrow \epsilon + d\epsilon$ .

Particle in box — side  $L$

Quantum mechanics

- particle represented by wavefn  $\psi$
- must obey boundary conditions

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Standing wave boundary conditions

Require  $\psi = 0$  at  $x, y, z = 0$   
 $= L$

Recall

$$\psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

$\swarrow$   
 normalis<sup>n</sup>.

At  $x, y, z = 0$

$\sin(\quad)$  ensures  $\psi = 0$

At  $x = L$

$$\psi = 0 \quad \text{for} \quad k_x \cdot L = \pi n_x$$

$$k_x = \frac{\pi n_x}{L}$$

$$k_y = \frac{\pi n_y}{L}$$

$$k_z = \frac{\pi n_z}{L}$$

where

$n_x, n_y, n_z$

are

positive

integers

$$\text{w/f } \psi = A \sin\left(\frac{\pi n_x}{L} x\right) \sin\left(\frac{\pi n_y}{L} y\right) \sin\left(\frac{\pi n_z}{L} z\right)$$

is standing wave in box specified

by quantum numbers  $n_x, n_y, n_z$ .

Representation in  $k$  space

Diagram — see sheet.

Points.

(i) Points at  $\frac{\pi n_x}{L}, \frac{\pi n_y}{L}, \frac{\pi n_z}{L}$

denote allowed states.

(ii) Characteristic spacing =  $\frac{\pi}{L}$

Note — if particle confined within

atomic dimension  $a$  —

spacing of states  $\sim \frac{\pi}{L}$



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For gases since enclosure  $L \sim 10^9 a$

Spacing of states very small.

Small spacing  $\longrightarrow$  classical case

$\pi/a$  spacing  $\longrightarrow$  quantum " .

Density of states in  $k$  space.

Number of states with  $k$  components in range

$$k_x \rightarrow k_x + dk_x$$

$$k_y \rightarrow k_y + dk_y$$

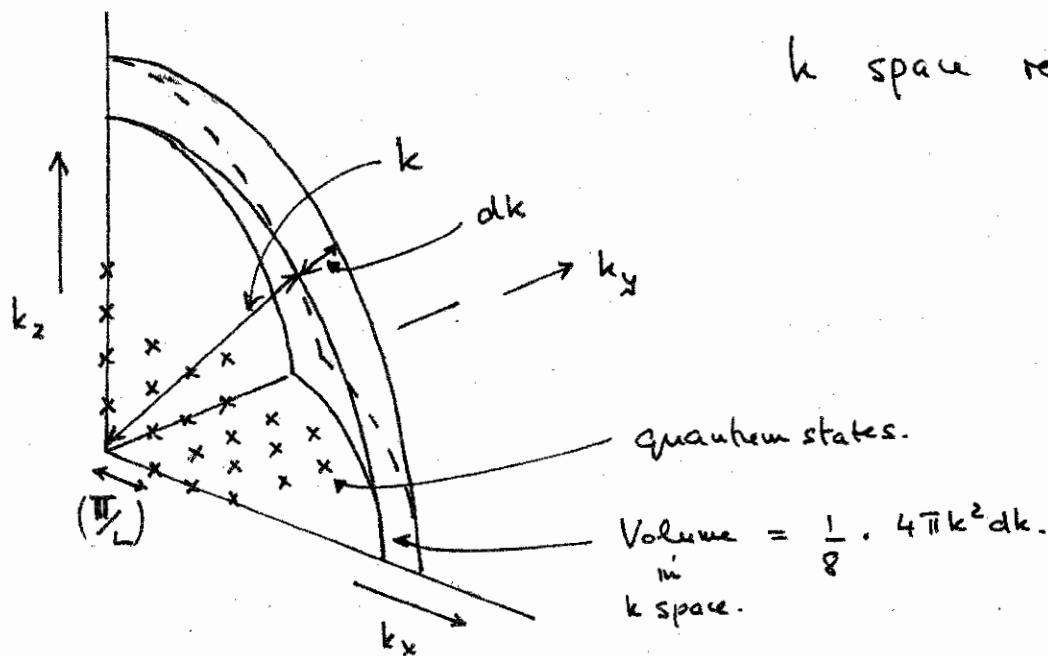
$$k_z \rightarrow k_z + dk_z$$

written as

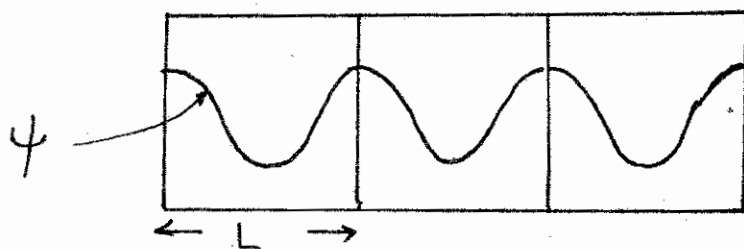
$$g(k_x, k_y, k_z) dk_x dk_y dk_z = \frac{dk_x dk_y dk_z}{(\pi/L)^3}$$

Volume  
of  $k$  space.

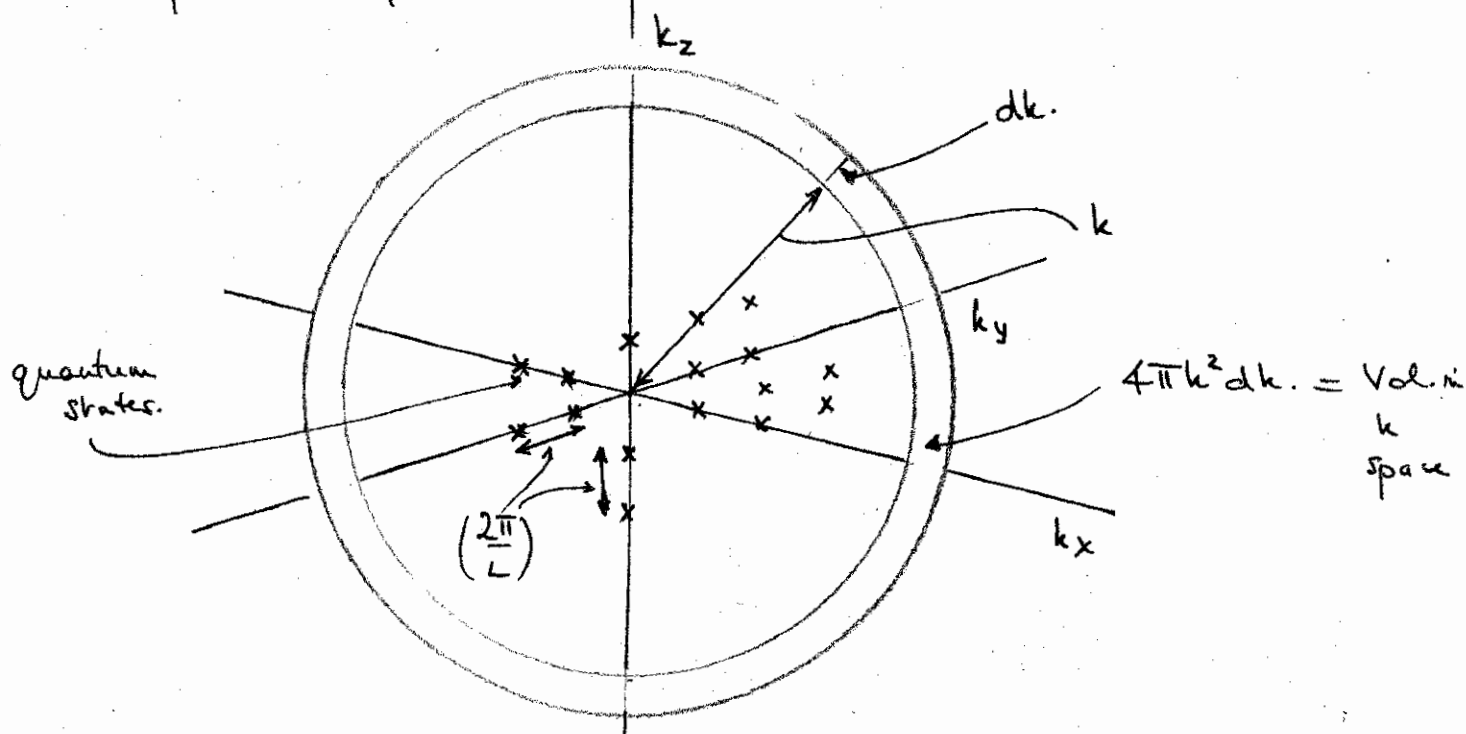
Standing wave boundary conditions.



Periodic Boundary conditions.



$k$  space representation



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Number of states with  $k \rightarrow k + dk$   
(all directions),

$$g(k) dk = \frac{1}{8} \cdot \frac{4\pi k^2 dk}{(\pi/L)^3}$$

where  $\frac{1}{8} \cdot 4\pi k^2 dk = \text{vol in } k \text{ space.}$  See sketch.

$$g(k) dk = \frac{L^3 \cdot 4\pi k^2 dk}{(2\pi)^3}$$

$$g(k) dk = \frac{V \cdot 4\pi k^2 dk}{(2\pi)^3}$$

Proved for case of  $V = L^3$  (cube)

but is generally true for  $V$   
of any shape.

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Travelling wave boundary conditions.

Moving particles — use wavefn  $\psi$ 

$$\psi = A \exp(ik_x x) \exp(ik_y y) \exp(ik_z z)$$

Boundary condition — periodic — see sheet.

Condition — w/f repeats in length of box.

For  $x$  dir'n.

$$A \exp(ik_x x) = A \exp(ik_x (x+L))$$

$$\cancel{\exp(ik_x x)} = \cancel{\exp(ik_x x)} \cdot \exp(ik_x L)$$

$$1 = \exp(ik_x L)$$

Requires  $k_x L = 2\pi n_x$   $k_x = \frac{2\pi n_x}{L}$

likewise  $k_y L = 2\pi n_y$   $k_y = \frac{2\pi n_y}{L}$

Now  $n_x, n_y, n_z = \pm 1, \pm 2, \dots$ Representation in  $k$  space — see sheet.

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Here

(i)  $n_x, n_y, n_z$  now take  $\pm$  integer values

(ii) Spacing  $(2\pi/L)$ .

Density of states

$$g(k) dk = \frac{4\pi k^2 dk}{(2\pi/L)^3}$$

$$= \frac{V \cdot 4\pi k^2 dk}{(2\pi)^3} \quad - \text{ as before}$$

Density of states in energy  $g(\epsilon) d\epsilon$

Want connection

$$g(k) dk \longrightarrow g(\epsilon) d\epsilon$$

Need relation between  $\epsilon$  and  $k$  - dispersion relation

This depends on system.

Particle mass  $m$  - all energy kinetic translation

Then  $\epsilon = \frac{p^2}{2m}$   $p = \text{momentum}$

Previous quantum mechanics  $p = \hbar k$

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

$$k = \left( \frac{2m\epsilon}{\hbar^2} \right)^{1/2}$$

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$$dk = \frac{1}{2} \left( \frac{2m}{\hbar^2} \right)^{1/2} \epsilon^{-1/2} d\epsilon$$

Then

$$g(k)dk = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 dk$$

$$g(\epsilon)d\epsilon = \frac{V}{(2\pi)^3} \cdot 4\pi \left( \frac{2m\epsilon}{\hbar^2} \right) \cdot \frac{1}{2} \left( \frac{2m}{\hbar^2} \right)^{1/2} \frac{d\epsilon}{\epsilon^{1/2}}$$

$$g(\epsilon)d\epsilon = \frac{V}{(2\pi)^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} d\epsilon$$

Points

(i) This for 3D system - easy to get

2D and 1D expressions

$$(ii) \epsilon = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

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$$\epsilon = \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2)$$

Energy spacing  $\Delta\epsilon = \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 \Delta n^2$

For He gas in box  $L = 0.3\text{m}$

$$\Delta n^2 = 1$$

$$m = 4 \times 1.66 \times 10^{-27} \text{ kg}$$

$$\Delta\epsilon = 3.8 \times 10^{-40} \text{ J} \equiv 2.4 \times 10^{-21} \text{ eV}$$

At  $300\text{K}$  then  $kT \equiv 0.025\text{eV}$

Thus  $kT \gg \Delta\epsilon$  classical limit.

(iii) Spin.

Particle with spin needs extra quantum numbers

If  $G$  different spin states - include in density of states

$$g(\epsilon) d\epsilon = G \cdot \frac{V}{(2\pi)^3} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} d\epsilon$$



Thermal distributions for different kinds of gas.

Gases — Large number of weakly interacting, indistinguishable particles confined in a macroscopic enclosure.

Different kinds

- (i) Fermi - Dirac gas
- (ii) Bose - Einstein gas
- (iii) Boltzmann gas.

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## Distribution

Variation of number of particles  $n_j$  in  
state of energy  $\epsilon_j$

or

probability of population  $f(\epsilon_j)$  for state of  $\epsilon_j$

## Method

Step 1. Single particle states — in gas  
very close together

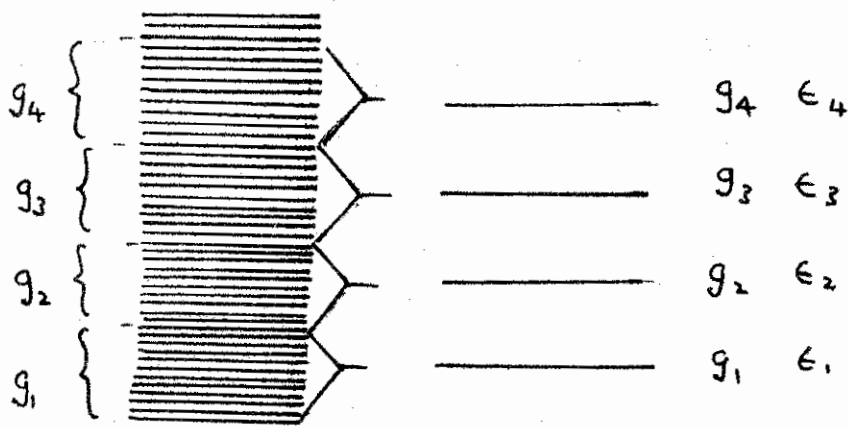
Step 2. Possible distributions

Convenient to clump energy states  $\epsilon_j$   
into wider spaced levels  $\epsilon_i$  each  
with degeneracy  $g_i$

Diagram — see sheet.

States to levels.

States (j)      Levels (i)



Distribution now  $\{n_i\}$        $n_i$  particles in level  $\epsilon_i$

Works if

- (i)  $g_i$  very large
- (ii) level spacing  $\Delta \epsilon_i \ll kT$ .

For case of He atoms (Guenault)

For  $g_i = 10^{10}$

Have  $\Delta \epsilon_i \sim 10^{-9} \cdot kT$ .

Conditions satisfied

Step 3 Count microstates for each possible distribution.

First - recap on Fermi-Dirac and Bose-Einstein particles.

Microstate of 2 indistinguishable particles -  $\psi(1,2)$

When particles exchanged  $1 \rightleftharpoons 2$

How is  $\psi(2,1)$  related to  $\psi(1,2)$  ?

Indistinguishable  $|\psi(2,1)|^2 = |\psi(1,2)|^2$

allows 2 solutions

$\psi_s(2,1) = +\psi(1,2)$  - symmetric

$\psi_A(2,1) = -\psi(1,2)$  - antisymmetric

Writing as weakly interacting particles 1, 2

in states a, b

$\psi(1,2)$  cannot be  $\psi_a(1)\psi_b(2)$  - not indistinguishable

Have to write

$$\psi_s(1,2) = \frac{1}{\sqrt{2}} \{ \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \}$$

$$\psi_A(1,2) = \frac{1}{\sqrt{2}} \{ \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \}$$

$\psi_s$  - symmetric - Bose Einstein particles

$\psi_A$  - antisymmetric - Fermi Dirac particles.

Crucial difference put  $a = b$

Bosons  $\psi_s = \sqrt{2} \psi_a(1)\psi_a(2)$

Fermions  $\psi_A = 0$

Pauli exclusion principle - no two fermions  
can occupy same quantum state

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## Examples

Fermions — spin  $\frac{1}{2}$ ,  $\frac{3}{2}$  ...

— electrons, protons, neutrons,  $\text{He}^3$  atoms

Bosons — spin 0, 1 ...

— photons, Cooper pairs,  $\text{He}^4$  atoms..

Return to deriving distribution for separate cases.

## Fermions.

Count microstates of  $n_i$  particles in level of  $\epsilon_i$  and degeneracy  $g_i$

$n_i$  ———  $g_i \epsilon_i$

Level has  $g_i$  states.

Each state occupied or unoccupied

$n_i$  states occupied

$(g_i - n_i)$  states unoccupied